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Communication: The highest frequency hydrogen bond vibration and an experimental value for the dissociation energy of formic acid dimer

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The highest frequency hydrogen bond fundamental of formic acid dimer, ν_{24} (B_u), is experimentally located at 264 cm^{-1} . FTIR spectra of this in-plane bending mode of $(\text{HCOOH})_2$ and band centers of its symmetric D isotopologues (isotopomers) recorded in a supersonic slit jet expansion are presented. Comparison to earlier studies at room temperature reveals the large influence of thermal excitation on the band maximum. Together with three B_u combination states involving hydrogen bond fundamentals and with recent progress for the Raman-active modes, this brings into reach an accurate statistical thermodynamics treatment of the dimerization process up to room temperature. We obtain $D_0 = 59.5(5)\text{ kJ/mol}$ as the best experimental estimate for the dimer dissociation energy at 0 K. Further improvements have to wait for a more consistent determination of the room temperature equilibrium constant. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4704827>]

INTRODUCTION

Accurate experimental determinations of the 0 K dissociation energy D_0 for hydrogen bonded clusters are rare. In the elementary case of HF dimer and its isotopologues, a direct measurement based on predissociation fragments became possible¹ after a spectroscopic absolute intensity analysis.² Recently, a similar fragment analysis provided the first reliable experimental value for water dimer.³ In considerably more complex systems with an aromatic chromophore, UV laser experiments can provide tight lower and upper bounds.^{4–6} For formic acid dimer, the prototype of a double hydrogen bridge, neither of these approaches is feasible. However, there is an increasingly complete spectroscopic data set of the dimer at low temperatures.^{7–10} Thus, one may quantify the dissociation equilibrium constant K_p near room temperature and combine this with the rovibrational partition function of the dimer from a complete jet-spectroscopic characterization of the low frequency modes⁹ and from rotational constants of the vibrational ground state.^{8,11} This reverses the strategy employed for HF dimer,¹² where the equilibrium constant K_p was estimated from D_0 and the partition functions.

Currently, the accuracy of this approach is limited for formic acid dimer around room temperature - both the equilibrium constant for dissociation and the vibrational partition function start to be affected by large amplitude motion, isomers,¹³ and metastable collision states,¹⁴ whereas larger clusters should not be a problem.¹⁵

The present work addresses the vibrational partition function issue by adding key missing elements for its accurate extrapolation to room temperature - the reliable band center determination for a poorly characterized low frequency mode and the observation of further combination bands involving

low frequency fundamentals. For this purpose, we present the first structured FTIR jet spectrum below 300 cm^{-1} of any hydrogen bonded complex or possibly even molecule.

EXPERIMENTAL

Formic acid (Sigma-Aldrich, >98%) or one of its isotopologues (Sigma-Aldrich, 95%, 98% D) was mixed with varying amounts of He (Linde, 99.996%) and collected in a 63 l reservoir at a pressure of 0.7 bar. From there, about 10% were dumped within 0.24 s (0.42 s) through 6 high-throughput magnetic valves into a 0.5 l pre-expansion volume. Expansion took place through a 600 mm long and 0.2 mm wide slit into a 23 m^3 vacuum chamber pumped at $2500\text{ m}^3/\text{h}$. The spatial and temporal core part of the expansion was probed through CsI optics by a mildly focussed Bruker IFS 66v FTIR beam modulated by a Si-coated Mylar beam splitter. The attenuation of the far infrared Globar radiation was monitored with a l-He cooled Si-bolometer, equipped with a 800 cm^{-1} cut-on filter and a polyethylene window, at a nominal sample rate of 20 kHz (40 kHz), corresponding to a single scan duration of 0.20 s at 4 cm^{-1} (0.37 s at 1 cm^{-1}) resolution. Recovery of the vacuum took place during a 50 s (65 s) waiting time before the next gas pulse. Details may be found in Ref. 16 and references cited therein.

FTIR SPECTRA AND THEIR ANALYSIS

Figure 1 shows the asymmetric hydrogen bond stretching or in-plane bending fundamental ν_{24} at 264 cm^{-1} (see Table S1 of supplementary material¹⁷ for a list of modes). It is the lowest frequency B_u mode and its Raman-active counterpart ν_{12} is observed at 242 cm^{-1} .⁹ At room temperature (trace a), it is strongly red shaded due to hot bands, as jet cooling (traces b and c) reveals. This explains why its band center had

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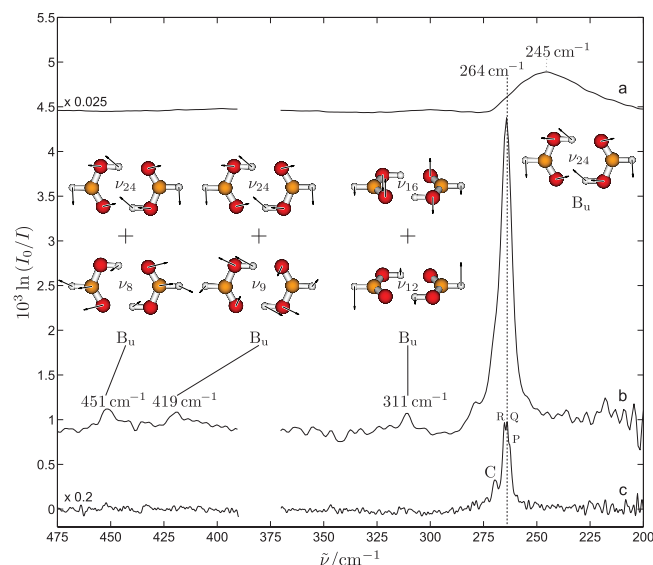


FIG. 1. Room temperature gas phase (a), low resolution jet (b) (4 cm^{-1} , 250 scans), and high resolution jet spectra (c) (1 cm^{-1} , 400 scans) of 0.4% HCOOH in He showing dimer absorptions. The band maximum of ν_{24} shifts upon cooling. It reveals rotational (P, Q, R branch) structure consistent with a rotational temperature of $10 \pm 5\text{ K}$ and small amounts of larger clusters (C) at higher resolution. At low resolution, combination bands $\nu_8 + \nu_{24}$, $\nu_9 + \nu_{24}$, and $\nu_{12} + \nu_{16}$ appear above the noise level. Monomer transitions are observed outside the $200\text{--}475\text{ cm}^{-1}$ window. The gap around 380 cm^{-1} is due to low transmission by the optical components.

previously been placed between 237 and 268 cm^{-1} ,^{10,18,19} with a preference for 248 cm^{-1} .^{9,18,19} The band marked C at 270 cm^{-1} is likely due to larger clusters formed in the jet, although a higher resolution study would be desirable. Observed band positions are listed in Table S2 of supplementary material¹⁷ for all isotopologues and spectra are shown in Fig. 1S of supplementary material.¹⁷

Weaker absorptions at 311 , 419 , and 451 cm^{-1} in the jet spectrum can be assigned to B_u combination bands based on previous Raman jet data⁹ for ν_8 , ν_9 , ν_{12} , and the present work (ν_{24}) as well as high resolution gas phase spectroscopy (ν_{16}).¹⁰ They provide important off-diagonal anharmonicity constants for these hydrogen bond modes, which are summarized in Table S3 of supplementary material.¹⁷ The fact that the $\nu_{12} + \nu_{16}$ combination band is additive with respect to the two fundamentals gives valuable support to the near-harmonic behaviour and correct wavenumber for the lowest frequency mode. Confirmation of the combination band at 395 cm^{-1} observed previously²⁰ is not possible due to a spectral transmission gap. The two combination bands involving ν_{24} show a more pronounced (1.5%) anharmonicity. A very weak feature in the Raman spectrum⁹ at 518 cm^{-1} can be attributed to $2\nu_{24}$, implying 2% diagonal anharmonicity for this mode.

VIBRATIONAL PARTITION FUNCTION

The goal is to determine the vibrational partition function of formic acid dimer $z_{vD}(T)$ as reliably as possible. The analysis focusses on $T = 296\text{ K}$, but lower temperatures are

even better suited for our approach. The starting point are the 24 anharmonic experimental fundamental transitions, in particular the low frequency ones which are thermally accessible. Our choice, including the value for ν_{24} obtained in the present work, is given in Table S1 of supplementary material.¹⁷ Infinite harmonic summation over all states building on these fundamental excitations yields $z_{vD}(296\text{ K}) = 42.5$, i.e., a vibrational ground state population of less than 2.5%. We estimate the total error in this vibrational partition function due to inaccurate band centers at ± 2 or less. The 4×10^5 levels up to $\approx 3000\text{ cm}^{-1}$ above the vibrational ground state account for about 97% of the 296 K population. We apply further anharmonic corrections using experimental data for some of them from this work and the literature.^{9,10} All other anharmonicities are roughly estimated, assuming $2x_{i,j}/(\tilde{\nu}_i + \tilde{\nu}_j) \approx -0.005$, i.e., consistently negative anharmonicity contributions of the same order of magnitude (0.5%) as experimentally determined in about a dozen low frequency cases. Based on this mixed model, the partition function at 296 K would increase by 11%. This may be too large because some positive off-diagonal anharmonicity contributions involving OH stretching and other intramolecular modes will partially cancel, rather than add together to the many negative contributions. On the other hand, it could be too low because we neglect singly hydrogen-bonded formic acid dimers,^{13,21,22} which start to become populated around 300 K. However, an energy difference of 20 kJ/mol and a 100-fold larger partition function due to a flatter potential energy hypersurface for these singly bound dimers would still not contribute more than 3% to z_{vD} . We consider the two errors to be comparable in size and conservatively estimate the size of the anharmonic correction at $11\% \pm 7\%$. Therefore, the final estimate for $z_{vD}(296\text{ K})$ is 47(4). For lower temperatures (see Table S5 of supplementary material¹⁷), the predicted vibrational partition function is more accurate.

The limiting values for the ν_{24} band center prior to this work⁹ ($248\text{--}268\text{ cm}^{-1}$) lead to a 4% difference in the final partition function, close to the now remaining uncertainty due to *all* 24 vibrations. A first complete set of low resolution gas phase fundamentals became available in the 1980s.^{20,23} Based on this set, the vibrational partition function was 30% higher than the present best value, largely because of the softening of the modes due to thermal excitation. Little was known about the corresponding anharmonic corrections, adding further to the error bar. The current best estimate of 47(4) for the vibrational partition function of formic acid dimer at 296 K is an order of magnitude more certain.

DISSOCIATION ENERGY

The dissociation equilibrium constant K_p for gaseous formic acid dimers (D) into ideally behaving monomers (M) at temperature T may be written as

$$K_p(T) = \frac{p_M^2}{p_D p^\circ},$$

where $p_{M,D}$ are partial pressures and $p^\circ = 10^5\text{ Pa}$ denotes the standard pressure. K_p is related to the molecular partition functions z_v , z_r , z_t for vibrational, rotational, and translational

motion and to the molar dissociation energy D_0 of the dimer at 0 K via

$$K_p(T) = \frac{z_{vM}^2 z_{rM}^2 z_{tM}^2}{z_{vD} z_{rD} z_{tD}} \exp(-D_0/RT).$$

According to this exponential relationship, a moderately accurate knowledge of the monomer and dimer partition functions and of the dissociation equilibrium for a given temperature determines the dissociation energy of formic acid dimer rather accurately.

The value of z_{rM} is based on the rigid rotor rotational constants.²⁴ For the rotational partition function of the dimer, we assume a symmetry number of 2 and neglect tunnelling splittings due to their small size,^{8,25} which is equivalent to a doubling of the states and the use of the D_{2h} symmetry number of 4. High resolution IR spectroscopy⁸ and four-wave mixing experiments¹¹ are within less than 0.5%. We start from the IR ground state result of z_{rD} (296 K) = $8.94(1) \times 10^4$ and round it up to $9.0(1) \times 10^4$ to account for rovibrational coupling in the low-lying vibrational states. z_{vM} is straightforward²⁶ within the infinite harmonic summation limit using experimental (anharmonic) fundamentals (1.12 for 296 K) and the lack of low-frequency modes renders the error of this approximation small, probably well within 1%.

We have analyzed a range of experimental determinations of K_p and converted them to the present standard pressure and 296 K, using the temperature dependence of the equilibrium constant determined by ΔH° (Table S4 of supplementary material¹⁷). These equilibrium constants fall in two broad categories - vapor density measurements²⁷ and spectroscopic monomer determinations.²⁶ The average value for $K_p p^\circ$ from the vapor density results (including photoacoustic resonance,²⁸ but excluding the data which need major temperature extrapolation) is about 265(20) Pa, whereas spectroscopy yields significantly higher values above 350 Pa. Combining the two types of data set with a double weight for the single reliable spectroscopic source, one arrives at 300(50) Pa. Having narrowed down the partition function uncertainty in the present work to less than 10%, this K_p discrepancy is now determining the accuracy of the resulting dissociation energy of formic acid dimer. Using the vapor density consensus for K_p , the best value for D_0 is 59.8(3) kJ/mol, whereas $D_0 = 59.1(4)$ kJ/mol follows from the spectroscopic monomer determination and its quoted error bar. A more accurate determination of the vibrational partition function would reduce the error bar by less than 0.2 kJ/mol. Our work thus calls for a more accurate determination of the equilibrium constant near or below room temperature.

All vapor density estimates assume an ideal mixture of (non-polar) dimers and (rather polar) monomers. The polarity of the monomers leads to a long-range influence on binary collisions, even if no dimer is formed along the trajectory. Normally, this would be absorbed into a “physical” negative second virial coefficient of the (monomeric) gas, but this is difficult to separate from “chemical” contributions due to the explicit dimerization.²⁹ Spectroscopy detects non-dimer forming collisions as pressure-broadened monomer lines. Therefore, it is expected that a dissociation constant

determined by monomer spectroscopy will be larger than a dissociation constant determined by the vapor density, where any contraction relative to the ideal monomeric gas must be blamed on dimers. One can summarize the situation by the following inequality between the measured total pressure p_t , the ideal gas monomer pressure p_M^i , and the (presumably close to ideal) non-polar dimer pressure p_D :

$$p_t < p_M^i + p_D.$$

A K_p method matching our experimental partition function would measure both the monomer and the dimer abundance spectroscopically, ignoring the total pressure. Vapor density measurements underestimate dissociation of dimers into polar monomers, whereas direct spectroscopic determination of p_M^i underestimates the quantity of dimers, as long as it infers it from p_t . Therefore, the discrepancy in K_p values (Table S4 of supplementary material¹⁷) is a physical one and the truth falls in between. This leads to the best estimate of $D_0 = 59.5 \pm 0.5$ kJ/mol.

One may argue that the enthalpy of dissociation at room temperature is a direct observable in the vapor density measurements as a function of temperature. We have extracted the 296 K values (Table S4 of supplementary material¹⁷), which typically fall in the 59 kJ/mol range, with the exception of the photoacoustic value of 62 kJ/mol. However, one should not compare these values directly with D_0 , as Fig. 2 shows. Due to the creation of six rotational and translational degrees of freedom upon dissociation, the enthalpy of dissociation initially increases with temperature as long as the hydrogen bond vibrations are not populated. When they become populated, this trend reverses and with

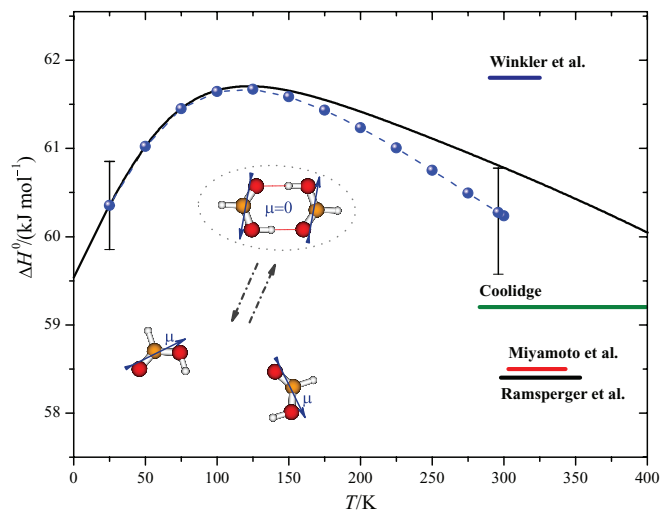


FIG. 2. Formic acid dimer dissociation enthalpy as a function of temperature according to the best D_0 value of 59.5(5) kJ/mol and the partition function up to 300 K. The full curve shows the infinite harmonic sum based on the anharmonic fundamentals from Table S1 of supplementary material,¹⁷ the dots include average anharmonic corrections $2x_{i,j}/(\bar{\nu}_i + \bar{\nu}_j)$ of 0.5% which are replaced by experimental values for the hydrogen bond modes listed in Table S3 of supplementary material.¹⁷ The error bar increases from 0 K to 300 K due to growing uncertainty in the anharmonicity contribution. One sees that vapor density measurements tend to underestimate the heat of dissociation, because the dissociated monomers still attract each other. However, one also should take into account the significantly larger temperature intervals used in those studies.

increasing anharmonicity influence, the dissociation enthalpy quickly drops below the D_0 value. Our model shows that this is almost the case at 296 K, with an estimated $\Delta H_{296\text{K}}^0$ value of 60.3(7) kJ/mol.

CONCLUSIONS

In an experimental approach to the dissociation energy of formic acid dimer at 0 K, we have removed the leading uncertainty about the vibrational partition function by completing the hydrogen bond mode information using far infrared supersonic jet spectroscopy. The last missing hydrogen bond fundamental, which stretches one hydrogen bond while it compresses the other, was located at 264 cm^{-1} . Infrared active combination bands further fix the 296 K vibrational partition function of the dimer at 47(4).

Combined with a critical analysis of the dissociation equilibrium constant at the same temperature, one arrives at a best value for D_0 of 59.5(5) kJ/mol. In simple terms, it makes a difference whether one measures the (partial) pressure of monomeric formic acid exerted on the wall or whether one determines its concentration by spectroscopy. A better method would determine both, the monomer and the dimer concentration, spectroscopically. This would open the way for an improved statistical dimerization analysis.³⁰

Among the carboxylic acid dimers, formic acid dimer is the most weakly bound.³¹ It is challenging to extend the present approach to acetic acid,^{15,31} because the methyl rotors add in a non-trivial way to the partition function and are affected by dimerization. It will also be interesting to uncover zero point energy effects in isotopologues of formic acid dimer.^{12,31}

For direct theoretical comparisons, it would be valuable to extract an experimental D_e value for formic acid dimer, i.e., to assess the anharmonic zero point energy difference on the order of 5–10 kJ/mol. This requires the full set of accurate experimental fundamentals and their anharmonicities. For the time being, theoretical benchmarking will have to include a calculated zero point energy correction. These calculations can be validated using the growing number of experimental fundamentals and anharmonicity constants available for formic acid dimer. Ultimately, this will lead to an experimentally refined potential energy hypersurface.³² The challenge to fix the zero point energy correction within less than 0.5 kJ/mol is that it consists of three contributions of similar size but different sign: The emergence of hydrogen bond modes in the dimer, the lowering of the OH stretching modes in the dimer, and the sum of all other, more subtle effects. However, one can safely assume that the true D_e value is bracketed by the coupled-cluster singles doubles

perturbative triples/aug'-cc-pVTZ results³³ with (62 kJ/mol) and without (72 kJ/mol) counterpoise correction.

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